CORRELATION OF DISSOCIATION ENERGY AND MOLECULAR CONSTANTS OF DIATOMIC MOLECULES

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ABSTRACT. A new relation, connecting dissociation energy (D_0), force constant of infinitesimal amplitude (k_e) and internuclear equilibrium distance (r_e) has been deduced from Sutherland's potential function. It is of the form $D_0 - k_e(A + Br_e + Cr_e^2)$, where A, B and C are contants and are same for a molecular group of similar diatomic molecules. The applicability of the relation has been shown in the case of about two hundred diatomic molecules forming nineteen molecular groups. Dissociation energy, hitherto unknown, of thirty diatomic molecules has also been predicted.

INTRODUCTION

During last four decades, numerous potential functions (Rittner, 1951; Varshni, 1957 and 1958a, Varshni *et al*, 1961) and empirical or semiempirical relaions connecting (Pauling, 1954; Varshni, 1958b, Somayajulu, 1960) the various molecular constants of diatomic molecules have been suggested.

Molecules having constant type of bonding are known to form a molecular group (Varshni, 1958b) or sequence (Somayajulu, 1960). For such a sequence the force constant for infinitesimal amplitude k_e is inversely proportional to the equilibrium internuclear distance r_e (Kratzer, 1920; Glasstone, 1936; Davies, 1949; Heath *et al*, 1950; Smyth, 1956), which in turn is inversely proportional to dissociation energy D_0 (Pauling, 1954). Combination of these relations lead Somayajulu (1960) to calculate the dissociation energy of molecules assuming $\frac{k_e r_e}{D_o}$ to be constant for a sequence and called it sequence constant S. Calculations show three main discrepancies : (1) values of S for different members of a sequence show much variation (Table, XII). (2) The estimated value of D_0 for the first member of the sequence differs much from the observed one in nearly all the cases. (3) The potential functions so far proposed (Varshni, 1957) do not lead to this relation. For example, the Linnett's function (1940, 1942)

$$U = a\, r^{-m} - b\, e^{-nr} \qquad \ldots (1)$$

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leads to the result (Somayajulu, 1960)

$$\frac{k_e r_e}{D_0} = mn\left[1+\frac{1}{(m-n\,r_e)}\right] \qquad \ldots (2)$$

We shall deduce new relation connecting the three molecular constants, k_e, r_e and D_0 from the Sutherland's potential function (1940), which is well established (Varshni, 1958).

We shall also use this relation to estimate D_0 values, hitherto unknown, in the case of many diatomic molecules.

NEW RELATIONS

A satisfactory potential function of a diatomic molecule satisfies the following conditions (Varshni, 1958a) :

$$U(r_e)-U(\infty) = -D_0 \qquad \ldots (3)$$

$$\left(\frac{dU}{dr}\right)_{r=r_e} = 0 \qquad \ldots (4)$$

and

$$\left(\frac{d^2U}{dr^2}\right)_{r=r_e} = k_e \qquad \ldots (5)$$

Applying these conditions on potential function

$$U(r) = \frac{a}{(r-d)^m} - \frac{b}{(r-d)^n} \qquad \ldots (6)$$

due to Sutherland (1940), we obtain

$$k_e = \frac{am(m-n)}{(r_e-d)^{m+2}} \qquad \ldots (7)$$

and

$$D_0 = \frac{a}{(r_e-d)^m}\left(\frac{m-n}{n}\right) \qquad \ldots (8)$$

From Equations (7) and (8) we get

$$\frac{D_0}{k_e} = \frac{n}{m}(r_e-d)^2 \qquad \ldots (9)$$

where m, n and d have been assumed to be constant for similar molecules. Equation (9) may be expressed in a general form

$$D_0 = k_e(A+Br_e+Cr_e^2) \qquad \ldots (10)$$

which is the new relation. A, B and C are constants, which may be expected to be the same for the molecules having similar bonding. The relation (10) has been applied to about two hundred diatomic molecules.

DATA AND PROCEDURE

The equilibrium internuclear distance r_e values are expressed in Å and are taken from the "Tables of Interatomic distances and configuration of molecules and Ions" (The Chemical Society, London, England, 1958) except where indicated. The r_e values in paranthesis are roughly estimated ones.

The values of force constant for infinitesimal amplitude k_e expressed in md/A have been calculated from molecular data given by Herzberg (1950) unless stated otherwise.

The observed values of dissociation energy $D_o°$, referred to 0°K, are expressed in electron volts. The values which are followed by H in paranthesis are taken from Herzberg's molecular data (1950). Similarly, G in paranthesis refers to data taken from Gaydon's book (1953) and that referred by Herzberg (1950) as Gaydon's data. D_0^0 values in paranthesis are uncertain ones.

The procedure to estimate D_0 values is very simple. Constants A, B and C for a molecular group are determined using $D_0°$, r_e and k_e values for three molecules for which these are known accurately. Having determined A, B and C mere substitution of k_e and r_e values in equation (10) yields D_0 values for other molecules of the group. T and S in paranthesis in Tables I to XX, refer to these estimated D_0 values and those estimated by Somayajulu (1960) respectively. 1a, 1b, 2a, ... etc. refer to the groups of the periodic table. 1a-7b refers to the molecular group of diatomic molecules formed by the combination of atoms belonging to 1a and 7b groups of the periodic table. Other symbols have similar meanings.

DISCUSSION

Study of the new relation connecting the dissociation energy D_0, force constant k_e and equilibrium internuclear distance r_e reveals that r_e values must be very accurately known, since higher powers of r_e appear in equation (10). While accurate k_e values, except in few cases, where they are estimated by Sheline method (1950) or method of Varshni and Majumdar (1955, 1956) or by any other method, are available for a large number of molecules, accurate r_e values are available only for few. Many unknown r_e values have been estimated by methods like Pauling's additivity of atomic radii, Schomaker-Stevenson equation (Gordy, 1946), Sheline method (1950), Varshni's relation (1958b) or Somayajulu's relation (1960). The use of these estimated r_e values is likely to produce divergence between

observed and estimated D_0 values. In certain cases the observed D_o° values are themselves uncertain where they are put in paranthesis. Large differences between observed and estimated D_0 values are expected in such cases. It is important to note that often spectroscopic, photochemical, thermochemical and electron impact appearance potential methods yield conflicting D_o° values. In most of the cases the convergence limit of bands with its adjoining continuum is not obtained. Birge and Spooner (1926) have suggested a method of extrapolation (Herzberg, 1950; Gaydon, 1953) to the convergence limit from the observed bands. In such cases D_0 values estimated by equation (10) may be used to assign most probable D°_o values. The unknown D_o° values of thirty diatomic molecules have also been estimated by this relation.

To show the applicability of the new relation, D_0 values estimated using this relation, indicated by (T) and those estimated by Somayajulu, indicated by (S), along with percentage errors in comparison with observed D_0° values are collected in Tables I to XIX. Values of average errors for different molecular groups are presented in Table XX. Close study of these tables reveals that the new relation yields much better results than Somayajulu's relation, because for twelve out of fifteen molecular groups the percentage error for (T) is less than that for (S). However, the average error for (T) in the case of 1a-H, 1a-7b and 4b-6b molecular groups is only 0.016%, 0.18%, and 1% higher than that for (S) respectively. Average error for molecules for which estimates of D_0 values have been made by new relation as well as by that of Somayajulu, are 1.76% and 2.78% for the former and latter respectively. This further confirms the superiority of the new relation. In the present study the scope of the applicability of the new relation is widened by including fifty more diatomic molecules belonging to 1b-7b, 2a-7b, 2b-7b and 4b-7b groups which have not been studied by Somayajulu.

TABLE I

Hydrides of 1a group

$A = 2.829$, $B = -1.533$, $C = 0.7798$

Molecule	r_e	k_e	D_0° Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
LiH	1.595	1.026	2.429[a], (2.5) (H)	2.429	0	2.427	−0.08
NaH	1.887	0.781	2.05±0 2(G), 2.2(H)	2.187	0	2.140	0
KH	2.244	0.5614	1.86±0.15(G), 1.86(H)	1.868	0	1.859	0
RbH	2.376	0.5148	1.7±0.2(G), (1.9)(H)	1.809	0	1.837	0
CsH	2.494	0.467	1.8±0.3(G), (1.9) (H)	1.728	0	1.800	−4
Average error %					0		0.016

a. Valasee (1957)

TABLE II

Hydrides of 1b group

$A = 4.030$, $B = -4.201$, $C = 1.583$

Molecule	r_e	$D_0°$ Observed		(S)		(T)	
				D_0 Cal.	Error%	D_0 Cal.	Error%
CuH	1.4631	2.2	2.7±0.3(G),<2.89(H)	2.77	0	2.797	0
AgH	1.6174	1.817	2.5(H), 2.3±0.1(G)	2.53	+1.2	2.502	+0.08
AuH	1.5237	3.138	4.1[a], 3.1(H)	4.12	+0.5	4.10	0
Average error %					0.57		0.03

The upper state is assumed to be $\tilde{\Sigma}+$, then it correlates with normal products and gives $D'' = 4.1$ ev.

TABLE III

Hydrides of 2a group

$A = 1.071$, $B = -1.002$, $C = 0.6671$

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 cal.	Error %
BeH	1.343	2.263	2.3±0.3(G), 2.2(H)	2.72	+4.6	2.041	0
MgH	1.731	1.275	2.0±0.5(G), ⩽2.49(H)	1.97	0	1.704	0
CaH	2.002	0.977	1.7(G), ⩽1.70(H)	1.75	+3.0	1.70	0
SrH	2.1456	0.854	1.65±1(G), ⩽1.68(H)	1.64	0	1.702	0
BaH	2.232	0.809	1.8±0.1(G), ⩽1.82(H)	1.61	−5.3	1.745	0
Average error %					2.6		0

TABLE IV

Hydrides of 3b group

$A = -0.1279$, $B = 1.095$, $C = -0.0029$

Molecules	r_e	k_e	$D_0°$ Obsrved	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
BH	1.233	(2.789)[a]	3.0±0.4(G),<3.51(H)	3.8	11.8	3.4	0
AlH	1.646	1.62	2.9±0.2(G), <3.06(H)	2.72	0	2.7	0
GaH	1.72[b]	1.42[b]	Unknown	2.49	—	2.088	—
InH	1.838	1.28	2.5±0.1(G), ⩽2.48(H)	2.4	0	2.40	0
TlH	1.87	1.143	⩽2.18(H)	2.18	0	2.18	0
Average errr %					3.0		0

a. Estimated using equation (10).
b. k_e recalculated by Sheline method (1950).

TABLE V

Hydrieds of 4b group

$A = -1.744$, $B = 3.020$, $C = -0.6891$

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
CH	1.12	4.484	3.47(G)(H)	3.86	+11.2	3.47	0
SiH	1.521[a]	2.39[a]	3.19±0.25[a]	2.79	−5.1	2.99	0
GeH	(1.66)[b]	1.87	unknown	2.28	—	2.56	—
	(1.591)[c]					2.46	
SnH	1.785	(1.469)[d]	2.13[e], <3.2(H)	2.06	−3.3	2.13	0
PbH	1.839	1.445	⩽2.04(H)	2.04	0	2.14	+4.9
Average Error %					4.8		1.2

a. Douglas (1957) b. Sheline (1950); c. Somayajulu (1960); d. Varshni (1958b); e. Assuming that the predissociation at 3.2 ev occurs into $Sn(^1D)+H(^2S)$.

TABLE VI

Hydrides of 5b group

$A = -0.8443$,, $B = 1.503$, $C = -0.0937$

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
NH	1.038	6.02	3.7±0.5(G), 3.8(H)	4.45	+6.0	3.70	0
PH	1.43	3.26	Unknown	3.32	—	3.63	—
AsH	1.58[a]	2.43[a]	Unknown	2.61	—	3.15	—
SbH	1.76[a]	2.05[a]	Unknown	2.5	—	3.10	—
BiH	1.809	1.708	2.5±0.3(G), 2.7(H)	2.2	0	2.67	0
Average error %					3.0		0

a. Sheline (1950)

TABLE VII

Hydrides of 6b group

$A = 0.5779$, $B = -0.4614$, $C = 0.4608$

Molecule	r_e	k_e	$D_0°$ Observe	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal	Error %
OH	0.971	7.791	0.393±0.03[a]	4.519	+2.6	4.395	0
SH	1.34[b]	4.193[c]	4.02>D″>2.88[b]	3.59	0	3.300	0
SeH	1.50[d]	3.18[a]	Unknown	2.99	—	2.934	—
TeH	1.69[d]	2.53[c]	Unknown	2.70	—	2.820	—
PeH	1.77[d]	2.1[d]	Unknown	—	—	2.53	—
Average rror%					1.3		0

a. Barrow (1956); b. Ramsay (1952); c. Leach (1954); d. Sheline (1950)

TABLE VIII

Hydrides of 7b group

$A = -0.8548 \quad B = 2.211, \quad C = -0.6788$

Molecule	r_e	k_e	D_0° Observe	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
FH	0.9171	9.655	5.8±0.1, ⩽6.40(H)	5.713	0	5.81	0
ClH	1.275	5.157	4.430(H), 4.431(G)	4.242	−4.2	4.43	0
BrH	1.4138	4.116	3.754(H)	3.754	0	3.756	+0.05
IH	1.604	3.141	3.06±0.01(G), 3.056(H)	3.251	+5.9	2.971	−2.6
AtH	1.68[a]	2.7[a]	unknown	—	—	2.539	—
Average error %					2.5		0.66

a. Recalculated by method of Sheline (1950).

TABLE IX

1a-1a group

$A = 0.8501, \quad B = 1.200, \quad C = 0.0127$

Molecule	r_e		D_0° Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
LiLi	2.672	0.2552	1.10±0.05(G), 1.03(H)	0.98	−4.9	1.059	0
NaNa	3.078	0.1717	0.75±0.03(G), 0.73(H)	0.76	0	0.800	+2.6
KK	3.923	0.0985	0.56±0.04[a], 0.51±0.05(G), 0.514(H)	0.555	0	0.567	0
RbRb	(4.18)[b]	0.082	0.49(H), 0.47±0.05(G)	0.493	0	0.490	0
CsCs	(4.50)[c]	0.06901	0.45(H), 0.45±0.04(G)	0.453	0	0.449	0
KLi	(3.29)[c]	(0.1487)[d]	Unknown	—	—	0.734	—
RbLi	(3.53)[c]	(0.1294)[d]	Unknown	—	—	0.679	—
CsLi	(3.83)[c]	(0.1094)[d]	Unknown	—	—	0.616	—
KNa	(0.1296)[c]	0.1296	0.62±0.03(G)	0.65	0	0.657	+1.0
CsNa	(3.75)[c]	0.108	Unknown	0.58	—	0.597	—
Average error %					0.8		0.6

a. Loonis *et al* (1932), b. Guggenheimer (1946), c. Gordy (1946), d. Varshni (1958b).

TABLE X

5b-5b group

$A = -0.4891$, $B = 0.9770$, $C = -0.1317$

Molecule	r_e	k_e	D°_0 Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
NN	1.0976	22.962	9.756(H)	11.0	+21.0	9.753	−0.3
PP	1.8943	5.556	5.03 or 4.12(H)	4.93	−2.0	4.938	−1.8
AsAs	2.08	4.069	⩽3.96(H)	3.96	0	3.96	0
SbSb	2.48	2.611	3.0±0.5(G)	3.03	0	2.935	0
BiBi	2.68	1.836	2.2 or 1.7(H)	2.3	+4.5	2.172	−1.3
PN	1.491	10.16	7.1±0.05[a], (6.3)(H)	7.09	0	6.86	−2.5
AsN	(1.59)[b]	7.926	5.0±1.0(G)	5.9	0	5.795	0
SbN	(1.79)[b]	6.564	5.5[c]	5.5	0	5.50	0
SbSb	(2.58)[b]	2.193	3.0±2.0(G), (3.0)(H)	2.65	0	2.531	0
Average error %					3.05		0.65

a. Huffman *et al*(1954); b. Somayajulu (1960), c. Assuming the limit of the upper state to correlate with $Sb(^2D)+(^4S)$.

TABLE XI

6b-6b group

$A = -1.3191$, $B = 1.943$, $C = 0.4059$

Molecule	r_e	k_e	D_0° Observed	(S)		(T)	
				D_0 Cal.	Error%	D_0 Cal.	Error%
OO	1.2074	11.765	5.1148±0.002[a]	6.436	+25.8	5.119	+0.4
SS	1.889	4.959	4.4(H), 4.6(G)	4.243	−3.6	4.474	+1.7
SeSe	2.152	3.612	⩽3.55(H)	3.52	0	3.548	0
TeTe	2.59	3.368	3.18(H)	2.78	−12.6	3.329	+ 4.7
SO	1.4933	3.921	5.358 or 4.212[b]	5.358	0	5.361	+ 0.06
SeO	(1.62)[c]	6.44	(5.4)(H), 3.5±1.0(G)	4.725	+ 5.0	4.915	− 9.0
TeO	(1.82)[c]	5.304	3.453(H)	4.372	+26.6	4.621	+34.1
Average error %					10.5		7.14

a. Brix *et al* (1954); b. Norrish *et al* (1959); c. Somayajulu (1960).

TABLE XII

7b-7b group

$A = -1.240$, $B = 1.646$, $C = -0.3241$

Molecule	S*	r_e	k_e	$D_0°$ Observed	(S)		(T)	
					D_0 Cal.	Error %	D_0 Cal.	Error %
FF	1.418	1.418	4.453	2.17 ± 0.2[a], < 2.75(H)	2.313	0	2.046	0
ClCl	1.488	1.988	3.286	2.475(H)(G)	2.393	−3.3	2.478	+0.1
BrBr	2.284	2.284	2.458	1.971(H)	2.056	+4.3	2.041	+3.5
II	2.729	2.667	1.721	1.5417(H)	1.681	+9.0	1.457	−5.5
FCl	1.629	1.628	4 483[b]	2.616 or 2.557(H)	2.719	+4.0	2.60	−0.6
FBr	1.756	1.755	4.095[c]	2.60 or 2.19(H)	2.637	+1.4	2.668	+2 6
FI	2.050	(2.05)[d]	3.64	2.87(G)	2.73	−4.9	2.81	−2.1
BrCl	2.141	2.138	2.717	2.26(H)	2.128	−5 8	2.173	3.8
ICl	2.321	2.321	(2.383)[d]	.152(H)c	2.026	−5.8	1.993	−7.4
IBr	2.434	2.434	2.064	1.817(H)	1.84	+1.2	2.749	−3.7
Average error %						4.0		2.9

Sequence constant $S^* = (r_e k_e / D_0)$

a. Caunt and Barrow (1949), b. Nielsen *et al* (1951), c. Durie (1951), d. Somayajulu (1960)

TABLE XIII

1a-7b group

$A = -0.3731$, $B = 1.978$, $C = -0.0972$

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
LiF	(1.59)[a]	(2.36)[b]	5.95 ± 0.2(G), ⩽6.6(H)	5.95	0	5.95	0
LiCl	(1.97)[c]	1.499[d]	5.0 ± 0.3(G)	4. 8	0	4.72	0
LiBr	2.17[c]	1.248[d]	4.35 + 0.3(G)	4 3	0	4.32	0
LiI	2.392[c]	0.9727[f]	3.5 ± 0.2(G)	3.69	0	3.70	0
NaF	(2.0)[c]	(1.465)[b]	4.65 ± 0.2(G), ⩽5.3(H)	4.65	0	4.68	0
NaCl	2.3606[c]	1.1[d]	4.24 ± 0.05(G)	4.15	+1.0	4.131	−1.4
NaBr	2.502[c]	0.959[d]	3.80 ± 0.1(G), 3.85(H)	3.81	0	3.804	0
NaI	2.7115[c]	0.7631[d]	3.07 ± 0.1(G), 3.16(H)	3.28	+3.5	3.18	+0.3
KF	2.55[g]	1.205[a]	5.0 ± 0.25(G)	5. 0	0	4.943	0
		1.24[a]				5.087	0
KCl	2.667[c]	1.02[a]	4.4 ± 0.05(G), 4.42(H)	4.32	−0.7	4.30	−1.1
KBr	2.821[c]	0.83[a]	3.94 ± 0.05(G), 3.96(H)	3.72	−4.4	3.68	−5.7
KI	3.048[c]	0.704[a]	3.32 ± 0.05(G), 3.33(H)	3.39	+0.6	3.35	0
RbF	(2.31)[c]	1.39[a]	5.35 ± 0.2(G),	5. 1	−1.0	5.113	−0.7
RbCl	2.787[h]	1.076	4.50 + 0.2(G), >3.96(H)	4.76	+1.3	4.718	+0.4
RbBr	2.945[c]	0.788[a]	4.0 + 0.25(G)	3.74	−0.02	3.63	−3.2
RbI	3.177[c]	0.633[a]	3.35 ± 0.1(G), 3.29(H)	3.33	0	3.122	−3.9
CsF	2.345[c]	1.451	5.5 ± 0.2(G)	5. 4	0	5.38	0
CsCl	2.906[c]	0.95[a]	4.6 ± 0.2(G)	4.38	−0.5	4.4	0
CsBr	3.072[c]	0.86[a]	4.1 ± 0.25(G), ⩾3.9(H)	4.19	0	4.12	0
CsI	3.315[c]	(0.665)[b]	3.4 ± 0.1(G), 3.3(H)	3. 5	0	3.40	0
Average error %					0.65		0.83

a. Barrow *et al* (1953), b. Somayajulu (1960), c. Rittner (1951), d. Rice *et al* (1937), e. Henig *et al* (1954), f. Klemperer *et al* (1957), g. Grabner *et al* (1950), h. Tirschka *et al* (1954).

TABLE XIV

1b-7b group*

$A = 6.718, \quad B = -6.125, \quad C = 1.599$

Molecule	r_e	k_e	$D_0°$ Observed	(T)	
				D_0 Cal.	Error %
CuF	1.743	3.32	(3.0)(H)	3.0	0
CuCl	(2.24)[a]	2.301	(3.0)(H)	2.4	−25.0
CuBr	(2.42)[a]	2.035	2.7+0.5(G), (2.5)(H)	2.57	0
CuI	2.40[b]	1.738	(3.0)(H), 1.9 ±0.2(G)	2.14	+2.0
	(2.63)[a]			2.91	−3.0
AgF	(1.998)[c]	(2.619)[d]	Unknown	2.26	—
AgCl	(2.42)[a]	1.832	3.1(H)	2.31	−25.5
AgBr	(2.59)[a]	1.637	2.6(H)	2.60	0
AgI	(2.81)[a]	1.453	2.98(H)	3.1	+4.0
AuCl	(2.48)[a]	2.564	3.5(H), 2.8±0.5(G)	3.50	0
Average error %					6.6

* D_0 values have not been calculated by Somayajulu (1960)
a. Calculated by Schomaker-Stevenson rule (see Gerdy, 1946)
b. Guggenheimer (1946), C. Varshni (1958b)
d. Varshni *et al* (1955, 1956),

TABLE XV

2a-7b group*

$A = -1.5383, \quad B = 1.623, \quad C = -0.0825$

Molecule	r_e	k_e	$D_0°$ Observed	(T)	
				D_0 Cal.	Error %
BeF	1.361	5.768	4.0+1.0(G)	3.0	0
BeCl	(1.7)[a]	3.025	3.0(G)	3.0	0
BeBr	(2.05)[b]	(2.145)[c]	Unknown	4.09	—
BeI	(2.33)[b]	(2.612)[c]	Unknown	4.69	—
MgF	(1.752)[a]	3.216	3.2±0.7(G)	3.37	0
MgCl	(2.29)[b]	1.815	(3.2)(H)	3.2	0
MgBr	(2.44)[b]	1.514	⩽3.35(H)	2.92	0
MgI	(2.72)[b]	(1.17)[a]	Unknown	2.65	—
CaF	(2.02)[a]	2.615	3.15(H)	3.67	+16.5
CaCl	1.86	1.504	⩽2.76(H)	1.79	0
CaBr	(2.70)[b]	1.274	(2.9)(H)	2.9	0
CaI	(2.98)[b]	1.051	(2.8)(H)	2.7	−3.6
SrF	(2.13)[b]	2.30	2.7±1.0(G), (3.5)(H)	3.55	0
SrCl	(2.68)[b]	1.345	(3.0)(H), 2.5±1.0(G)	3.0	0
SrBr	(2.83)[b]	1.146	(2.8)(H)	2.8	0
SrI	(3.11)[b]	0.9231	2.2(H)	2.5	+13.6
BaF	(2.22)[b]	2.161	(3.8)(H)	3.62	−4.7
BaCl	(2.77)[b]	(1.162)[d]	(2.7)(H)	2.7	0
BaBr	(2.92)[b]	1.109	(2.8)(H)	2.8	0
BaI	(3.20)[b]	(0.874)[c]	Unknown	2.44	—
Average error %					2.9

* D_0 values have not been calculated by Somayajulu (1960).
a. Varshni (1958b),
b. Margrave (1954),
c. estimated by method of Varshni *et al* (1955, 1956)
d. estimated by equation (10).

TABLE XVI

2b-7b group*

$A = -0.9328$, $B = 1.849$, $C = -0.5073$

Molecule	r_e	k_e	$D_0°$ Observed	(T)	
				D_0 Cal.	Error %
ZnF	(1.59)[a]	(3.441)[b]	Unknown	2.496	—
ZnCl	(1.945)[b]	2.046	2.5±1.0(G)	1.523	0
BnBr	(2.136)[b]	(1.661)[c]	Unknown	1.165	—
ZnI	(2.30)[b]	1.25	1.8±0.6(G)	0.800	−33.3
CdF	(1.723)[b]	(2.74)[b]	Unknown	2.045	—
CdCl	(2.094)[b]	1.716	2.2±1.0(G)	1.225	0
CdBr	(2.248)[b]	1.455	2.8±1.0(G)	1.960	0
HgF	(1.74)[a]	2.406	(1.8)(H), 1.4±0.5(G)	1.798	0
HgCl	(2.23)[b]	1.502	1.0(H)	1.000	0
HgBr	2.44[a]	1.180	0.7(H)	0.7	0
HgI	2.55[a]	0.7223	0.30±0.05(G), 0.36(H)	0.35	0
Average error %					4.2

* D_0 values have not been calculated by Somayajulu (1960),

a. Guggenheimer (1946),

b. Varshni (1958b),

c. estimated by method of Varshni *et al* (1955, 1956)

TABLE XVII

3b-7b group

$A = -1.0879$, $B = 2.279$, $C = -0.4596$ for 7b-B group

$A = -5.407$, $B = 6.226$, $C = -1.204$ for the rest

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
BF	1.262	8.043	8.5±0.5(G)	8.50	0	8.5	0
BCl	1.716	3.473	5.1±0.4(G)	5.0	0	5.1	0
BBr	1.887	2.665	4.2±0.2(G), (4.1)(H)	4.21	0	4.15	0
BI	(2.17)[a]	(1.86)[b]	Unknown	3.3	—	3.24	—
AlF	1.654[c]	4.191[d]	6.7±0.3(G)	6.83	0	6.68	0
AlCl	2.138	2.078	5.0±0.2(G)	4.38	−8.7	5.0	0
AlBr	2.295	1.692	4.3±0.3(G)	3.83	−4.2	4.29	0
AlI	2.53[e]	1.31	3.7±0.7[f]	3.3	0	3.47	0
GaF	1.775[c]	3.41[g]	6.2±0.03[g]	5.96	−3.4	6.32	+ 1.6
GaCl	2.208[c]	1.821	4.99±0.02(G)	3.96	−20.3	4.5	− 9.4
GaBr	(2.35)[a]	1.516	3.5±0.8(G)	3.5	0	3.9	0
GaI	(2.50)[b]	1.233	2.9±0.2(G), 2.88(H)	3.0	0	3.25	+4.8
InE	1.985[c]	2.74[g]	5.41(G)	5.36	−0.9	6.05	+11.8
InCl	2.401[c]	1.591	4.5±0.1(G)	3.76	−14.5	4.15	-5.7
InBr	2.541[c]	1.366	3.4±0.2(G)	3.42	0	3.60	0
InI	(2.72)[e]	1.114	2.8±0.2(G)	3.0	0	2.92	0
TlF	(1.93)[a]	2.31	4.75±0.2(G)	4.74	0	4.91	0
TlCl	2.541[c]	1.453	<3.19(H)	3.64	+14.1	2.16	0
TlBr	2.68	1.26	3.2±1(G), 3.19(H)	3.25	0	3.32	+0.6
TlI	2.814	1.038	2.8±0.23[f], 2.64(H)	2.88	0	2.68	0
Average error%					3.5		1.8

a. Margrave (1954), b. Varshni (1958b), c. Barrow *et al* (1957), d. Naude *et al* (1955),

e. Guggenheimer (1946), f. Brewer *et al* (1950), g. Barrow *et al* (1954), h. estimated by Schomaker-Stevenson rule (see Gerdy, 1956).

TABLE XVIII

4b-7b group*

$A = -3.346$, $B = 3.768$, $C = -0.6664$

Molecule	r_e	k_e	$D_0°$ Observed	(T)	
				D_0 Cal.	Error %
CF	1.271[a]	7.406[a]	Unknown	2.707	—
CCl	1.73[b]	3.766	Unknown	4.440	—
CBr	(1.901)[c]	(2.925)[c]	Unknown	5.567	—
CI	(2.175)[c]	(2.175)[c]	Unknown	3.680	—
SiF	(1.603)[c]	4.892	4.8(H)	4.8	0
SiCl	2.00[b]	2.624	4.0(H)	4.0	0
SiBr	2.15[b]	2.213	3.7(H)	3.7	0
SiI	(2.459)[c]	(1.658)[c]	Unknown	3.14	—
GeF	(1.670)[c]	3.925	(4.9)(H)	4.3	−10.2
GeCl	(2.08)[b]	2.323	(4.0)(H)	3.74	−6.5
GeBr	(2.29)[b]	1.971	(3.0)(H)	3.5	+16.7
GeI	(2.558)[c]	(1.523)[c]	Unknown	2.94	—
SnF	(1.82)[b]	3.278	3.9(H)	4.28	+9.7
SnCl	2.32[b]	1.976	3.6(H), 3.2±0.5(G)	3.6	0
SnBr	2.44	1.726	(3.0)(H)	3.247	+8.2
SnI	(2.682)[c]	(1.373)[c]	Unknown	2.7	—
PbF	(2.01)[b]	2.630	⩽4.5, 3.47(H)	4.04	0
PbCl	2.43[b]	1.627	2.6±0.4(G), 3.1(H)	3.05	−1.7
PbBr	2.60[b]	1.449	2.9(H), 2.2+0.4(G)	2.82	−2.7
PbI	(2.86)[c]	1.194	2.8(H)	2.4	−14.3
Average error %					5.4

*D_0 values have not been calculated by Somayajulu (1960).

a. Rosen (1951),

b. Guggenheimer (1946),

c. Varshni (1958b).

TABLE XIX

4b-6b group

$A = -0.6803$, $B = 1.317$, $B = -0.1742$

Molecule	r_e	k_e	$D_0°$ Observed	(S)		(T)	
				D_0 Cal.	Error %	D_0 Cal.	Error %
CO	1.1282	19.02	11.11(G)	11.11	0	11.115	+ 0.04
CS	1.534	8.488	7.9[a], 7.2±1.0(G)	7.90	0	7.907	0
CSe	1.669	6.585	6.8(H)	6.67	−1.9	6.8	0
CTe	(1.949)[b]	4.945[c]	Unknown	5.85	—	6.066	—
SiO	1.510	9.247	8.0±1.0(G), 8.9±0.27[d]	8.09	0	8.436	0
SiS	1.9288	4.937	6.4±0.5(G)	5.78	−2.0	5.983	0
SiSe	(2.14)[e]	4.094	5.3±0.5(G), 5.8(H)	5.32	0	5.490	0
SiTe	(2.34)[e]	3.130	4.5±0.3(G)	4.44	0	4.521	0
GeO	1.6507	7.525	6.75±0.28[d], 6.9(H)	7.20	−3.1	7.677	+10.0
GeS	(2.06)[e]	4.358	5.66±0.13(G), 5.6(H)	5.45	−1.4	5.643	0
GeSe	(2.19)[e]	3.743	4.98±0.25(G)	5.02	0	5.128	0
GeTe	(2.39)[e]	2.902	4.1±0.4(G)	4.13	0	4.278	0
SnO	1.838	5.615	5.9[a]	5.98	+1.3	6.474	+ 9.7
SnS	(2.26)[e]	3.536	4.81±0.28[f]	4.85	0	4.979	0
SnSe	(2.37)[e]	3.066	5.54[g], 4.6(H)	4.45	−2.0	4.5	−0.9
SnTe	(2.57)[e]	2.439	4.1[g]	3.81	−7.1	3.798	−7.3
PbO	1.922	4.557	(4.3)(H)	5.07	+17.9	5.508	+28.1
PbS	2.395	2.992	4.6[h], (4.7)(H)	4.35	−5.4	4.42	−3.9
PbSe	(2.53)[e]	2.595	3.5±1.0(G), 4.27[h]	3.98	0	3.992	0
PbTe	(2.73)[e]	2.086	3.5(H)	3.46	−1.1	3.378	−3.5
Average error					2.3		3.3

a. Thermochemical values, b. Varshni (1958b), e. Rosen (1951), d. Barrow *et al* (1954), e. Guggenheimer (1946), f. Barrow *et al* (1953), g. Vago *et al* (1946), h. Vago *et al* (1948).

et al (1948).

TABLE XX

Average percentage errors

Molecular Group	(S)	(T)
1a–H	0	0.016
1b–H	0.57	0.03
2a–H	2.6	0
3b–H	3.0	0
4b–H	4.9	1.2
5b–H	3.0	0
6b–H	1.3	0
7b–H	2.5	0.66
1a–1a	0.8	0.6
5b–5b	3.05	0.65
6b–6b	10.5	7.14
7b–7b	4.0	2.9
1a–7b	0.65	0.83
1b–7b	—	6.6
2a–7b	—	2.9
2b–7b	—	4.2
3b–7b	3.5	1.8
4b–7b	—	5.4
4b–6b	2.3	3.3

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REFERENCES

Barrow, R. F., Drummond, G, and Rowlinson, H. C., 1953, *Proc.Phys. Soc.*, London, ***A66***, 885.

Barrow, R. F. and Caunt, A. D., 1953, *Proc. Roy Soc.*, London, ***A219***, 120.

Barrow, R. F. and Rowlinson, H. C., 1954, *Proc. Roy. Soc.*, London, ***A224***, 374.

Barrow, R. F., 1956, *Arkiv Fysik*, **11**, 281.

Barrow, R. F., Dodsworth, P. G., and Zeeman, P. B., 1957, *Proc. Phys. Soc.*, London, ***A* 70, 34.**

Birge, R. T. and Sponer, H, 1926, *Phys. Rev.*, **28**, 259.

Brewer, L., 1959, *J. Chem. Phys.*, **31**, 1143.

Brix, P. and Herzberg, G., 1954, *Cand. J. Phys.*, **32**, 110.

Caunt, A. D. and Barrow, R. F., 1949, *Nature*, **164**, 753.

Cottrell, T. L., 1958, The Strengths of the Chemical bends, 2nd. ed. (Butterworths Scientific Publications Ltd., London)

Davies, M., 1949, *J. Chem. Phys.*, **17**, 374.

Douglas, A. E., 1957, *Cand. J. Phys.*, **35**, 71.

Durie, R. A., 1951, *Proc. Roy. Soc.*, London, *A***207**, 388.

Gaydon, A. G., 1953, Dissociation Energies, (Chapman and Hall Ltd., London).

Glasstone, S., 1936, Recent Advances in Physical Chemistry, 3rd. ed. (P. Blakiston's Son and Co. Inc., Philadelphia).

Gordy, W , 1946, *J. Chem. Phys* , **14**, 305

Guggenheimer, K M , 1946, *Proc. Phys. Soc* , London, **58**, 456

Grabner, L and Hughes, V , 1950, *Phys Rev* , **79**, 819

Health, D F , Linnett, J W , and Wheatley, P J , 1950, *Trans Faraday Soc* , **46**, 137

Herzberg, G , 1950, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules, 2nd ed (D Van Nostrand Company, New York)

Honig, A , Mandol, M , Stitch, M L , and Townes, C H , 1954, *Phys Rev* , **96**, 629

Huffman, E. O., 1954, *J. Am. Chem. Soc* , **76**, 6239

Klemperer, W and Rice, S A , 1957, *J Chem Phys* , **26**, 618

Kratzer, A , 1920, *Z Physik*, **3**, 289

Leach, S , 1954, *J. Chem. Phys.*, **22**, 1261

Linnett, J W , 1940, *Trans. Faraday Soc* , **36**, 1123

Linnett, J W , 1942, *Trans. Faraday Soc* , **38**, 1

Loomis, F W and Nausbaum, R. E., 1932, *Phys. Rev.*, **39**, 89.

Margrave, J. L., 1954, *J. Phys. Chem.*, **58**, 258.

Naude, S. M., and Huge, T. J., 1955, *Cand. J. Phys.*, **33**, 573

Nielsen, A. H., and Jones, E. A., 1951, *J. Chem. Phys.*, **19**, 1117.

Norrish, R. G. W. and Oldershaw, G. A., 1959, *Proc. Roy. Soc* , London, *A***249**, 498

Pauling, L., 1954, *J. Phys. Chem.*, **58**, 662.

Ramsay, D. A., 1952, *J. Chem. Phys.*, **20**, 1920.

Rice, S. A. nd Klemperer, W., 1957, *J. Chem. Phys.*, **27**, 643.

Rittner, E. S., 1951, *J. Chem. Phys.*, **19**, 1030.

Rosen, B., 1951, Donnees spectroscopiques Concernant les Molecules Diatomiques (Hormann and Cio Depositaires, Paris.).

Sheline, R. K., 1950, *J. Chem. Phys.*, **18**, 927.

Smyth, R. P., 1956, *J. Phys. Chem.*, **60**, 1293.

Somayajulu, G. R., 1960, *J. Chem. Phys.*, **33**, 1541.

Sutherland, G. B. B. M., 1940, *J. Chem. Phys.*, **8**, 161.

Trischka, J. W. and Braunstein, B., 1954, *Phys. Rev.*, **96**, 968.

Vago, E. E., and Barrow, R. F., 1946, *Proc. Phys. Soc.*, London, **58**, 538.

Vago, E. E. and Barrow, R. F., 1948, Vistor Henri Commemorative Volume (Maison Desoeur, Liege, Belgium).

Valasco, R., 1957, *Can. J. Phys.*, **35**, 1204.

Varshni, Y. P., and Majumdar, K., 1955, *Indian J. Phys.*, **29**, 38, 285.

Varshni, Y. P., and Majumdar, K., 1956, *Indian J. Phys.*, **30**, 303.

Varshni, Y. P., 1957, *Revs. Mod. Phys.*, **29**, 664.

Varshni, Y. P., 1958, *J. Chem. Phys.*, **28**, a. 1078, b. 1081.

Varshni, Y. P. and Shukla, R. C., 1961, *J. Chem. Phys.*, **35**, 582.